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The Effect of the Proportion and Clay Mineralogical Composition on the Rheological Properties of the Raw Clay and the Sodium Carbonate Treated Clay Suspensions

Abderazak Elhechi[a], *, Olfa Ben Amor[a], Riadh Abidi[a], and Ezzeddine Srasra[b]

[a] *University of Tunis El Manar, Faculty of Sciences, Laboratory of Geodynamics, Geonumeric and Geomaterials, Tunis, 2092 Tunisia*

[b] *National Center for Research in Materials Sciences, Laboratory of Composite Materials and Clay Minerals, Soliman, 8027 Tunisia*

**e-mail: abderazak_elhechi@yahoo.fr*

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Abstract—The X-ray diffraction, infrared spectroscopy, chemical analysis, and cation exchange capacities are the most common techniques used for the physico-chemical study and characterization of clays. All of these used in the present study showed that the Tunisian clay samples collected from Zaghouan area (Zg_1, Zg_2, and Zg_3) and Hawaria area (Ha1, Ha_2, and Ha_3) consisted of illite, kaolinite, and smectite associated with quartz, K-feldespar, calcite, and dolomite. The chemical analysis revealed that Al_2O_3 is relatively high in the Ha_2 sample. The CaO rate was high (5.08 and 7.16 wt %) for Ha_3 and Zg_3 samples. To demonstrate the impact of clay mineralogical composition on the rheological properties, six samples were used to prepare the mixed clay aqueous suspension. Its effect depends on the proportion of the 2:1 phyllosilicate, especially smectite, as well as on the rheological properties of the blank clay suspensions and of Na_2CO_3 treated ones. Calcite forms large agglomerations with clays minerals, which prevents flocculation. The negative charges in the tetrahedral layers were generated by the substitution of Si^{4+} with Al^{3+}, and they were compensated by the interlayer exchangeable cations. Therefore, the interlayer hydration leads to an increase of the dispersion of clay particles and rheological properties.

Keywords: clay suspensions, rheological behavior, sodium carbonate, physicochemical characterization

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INTRODUCTION

From the point of view of their physico-chemical properties, the mineralogical composition, rheological properties, the cation exchange capacity (CEC), structure, texture, and a high specific surface, clay minerals seem to be important for many engineering and industrial application fields. They are widely used as raw materials or as basic components in petroleum industries, industrial ceramics, cements manufacture, paper production, cosmetics, pharmaceuticals, as bonding agents for foundry molding sands, ceramic membranes, and they used for water and wastewater treatment through adsorption and filtration methods [1–8].

Minerals with 2 : 1 and 1 : 1 structures represent two groups of the most widely spread clay minerals. The 2 : 1 phyllosilicate group is characterized by two tetrahedral silicon layers overlying an octahedral aluminum layer. For the 1:1 phyllosilicate group, just one tetrahedral silicon layer is superposing an octahedral aluminum layer. Those minerals differ from each other by many properties. Indeed, the 2 : 1 phyllosilicate illite and smectite, especially the smectite minerals, have a wide interlayer spacing, which allows them to absorb a large amount of water and permits considerable swelling [9]. Contrary to that, the 1 : 1 phyllosilicate kaolinite contains a very narrow interlayer spacing.

The purpose of the present study was to clarify the effect of the clay mineralogical composition on the rheological behavior of the raw clay and of that after the Na_2CO_3 addition to the suspensions. The adjuvants have been particularly used in many colloidal suspensions to flocculate and stabilize the clay particles, an under-deflocculated slip or over-deflocculated slip can cause defects [10]. To obtain a suspension of an adequate density, three clay properties must be respected such as mineralogical and chemical compositions and clay concentration. Eventually, fine particles disperse and retard the free settling of the clay mineral. This dispersion is necessary for the stabilization of the suspension and an increase in viscosity [11]. Therefore, the clays applied in ceramics have to meet special technological requirements such as fast disper-

sion and the stability of clay particles in water. Meeting these criteria, clay has emerged as essential component of ceramic molding. Depending on various physico-chemical parameters, structure, and texture, clay mineral dispersions form viscous solutions are important. Dispersion of colloidal particles of 2 μm size is an important process for ceramic particles used in the slip preparation as they have a suitable rheological behavior. Moreover, clay minerals exhibit excellent surface properties and high chemical stability, which is very suitable for applications in the process of ceramic molding of articles. The investigations about clay mineral dispersions deal with the clay phases behavior and, in particular, with their structure and texture. Clay dispersions show several viscosity states according to solids concentration and orientation of the colloidal clay mineral layers. The repulsive and attractive electrostatic forces and the van der Waals forces control the arrangement of clay mineral layers. The effects of the exchangeable cations on the morphology and the clay dispersion are monitored by the Na/Ca ratios and the amount of the cations originally present in clay. Thus, the clay swelling is affected by the nature of the exchangeable cations in the interlayer space, by the layer charge, and by the particle size [12, 13].

GEOLOGICAL AND SEDIMENTOLOGICAL SETTINGS

The Tunisian clay samples for the physico-chemical and rheological studies were collected from two different sedimentary basins in Tunisia, which included Cap Bon and Zaghouan area (Fig. 1). The first investigated area is located at the wide plain of the Hawaria region in Cap Bon. The sedimentary basin is characterized by a large outcrop of a middle Miocene clay deposit ranging from Langhian sup to Tortonian, attribute to the Saouaf formation. The thickness can reach 2000 m in particular localities formed by an abundance of green clay with alternating sandstones [14, 15]. Three representative clay samples (Ha_1, Ha_2, and Ha_3) were gathered from the bottom to the top of the Saouaf formation (Fig. 2). For the second investigated area, in the Zaghouan region, where the clay sediments—objects of study here, belong to the Early Cretaceous series of the M'charga formation. M'charga formation, about 3000 m thick, is dominated by grey to green claystones interbedded with carbonate beds and sandstones [16–18]. Other three representative clay samples (Zg_1, Zg_2, and Zg_3) were gathered from the bottom to the top of the M'charga formation (Fig. 2).

MATERIALS AND METHODS

The structural properties of the investigated raw clays were determined by the following steps: the determination of the mineralogical composition of samples by a Philips X-ray diffractometer, with a monochromatic wavelength λCu Kα, at 2 range of 2–65°; the semi-quantitative analysis of different phases with the software X'Pert High Score Plus; the extraction of the clay fraction (<2 μm) from centrifugation and its treatment with HCl (1 N) for the dissolution of carbonates. Then the relative abundances of the non-clay minerals were deduced from the heights of the main reflections. For the clay minerals, the quantification was based on the measurements of the reflections areas in the diffractograms using the correcting factors [19, 20]. Next, the chemical composition of the studied materials was analyzed by the inductively coupled plasma-mass spectrometry. The chemical analyses of the major oxides composition (wt %) of the tested clays revealed SiO_2, Al_2O_3, Fe_2O_3, K_2O, Na_2O, CaO, MgO, and SO_3 and the loss on ignition. Then the Fourier-transform infrared spectroscopy (FT-IR) measurements were carried out using a FT-IR spectrophotometer with the waves of 4000 to 400 cm^{-1} at a resolution of 1 cm^{-1} with KBr pellets (sample/KBr approximately 1/200) and using a hydraulic press at 10 ton cm^{-2}. Next, the particles sizes distribution of the raw clays was determined by a laser granulometer Malvern Mastersizer 2000, with a particles size measurement less than 100 μm. Then, the CEC values were determined using the copper complex method [21]. Finally, the measurement of the rheological behavior of suspensions was performed using a viscometer.

RESULTS AND DISCUSSION

X-Ray Diffraction

The X-ray diffraction (XRD) patterns (Fig. 3, Table 1) revealed that the examined samples were rich in clay minerals. Indeed, the percentages ranged from 50 to 60 wt %. In all samples, illite and kaolinite were the predominant crystalline phases. The illite, kaolinite, and smectite phases were identified with the reflection at 9.8, 7.16, and 14 Å, respectively. The major non-clay minerals that were found were quartz, feldspars, and calcite. They were identified with the reflection at 3.32, 3.21, and 3.03 Å, respectively. The percentages of illite ranged from 10 to 47 wt %, and the kaolinite rates varied from 12 to 40 wt % for all samples. Smectite was also obtained, but with percentages that did not exceed 18 wt %. The quartz percentages varied from 24 to 31 wt % for all samples. Dolomite was also found, but in low percentages in all samples. However, calcite was found with relatively high percentages of 10 and 12 wt % for Zg_1 and Zg_3 clay samples, respectively.

Chemical Analyses

The results of the chemical analyses of the raw clays studied (Table 2) revealed the presence of several ionic species. All clays were formed mainly of SiO_2 and

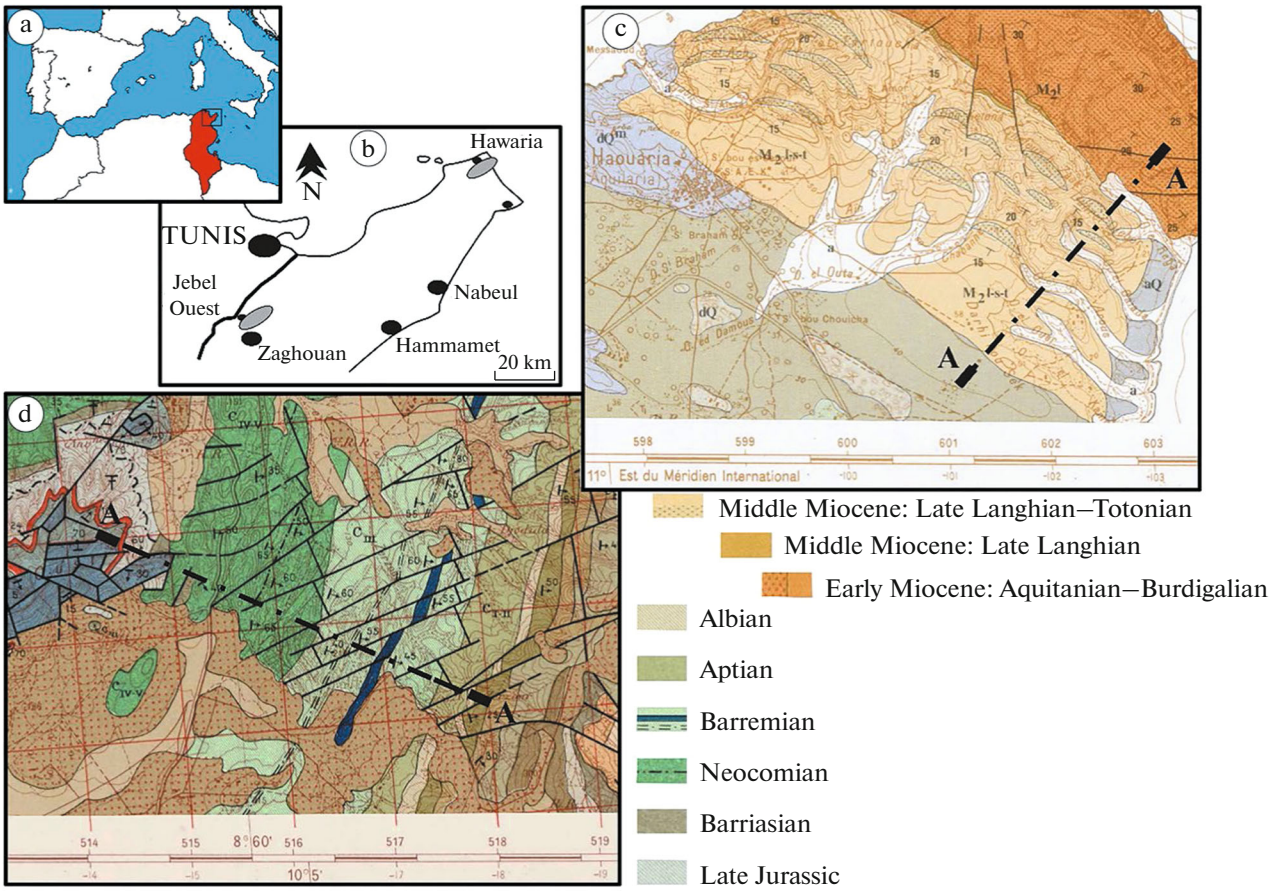

Fig. 1. (a) Tunisian geographical situation, (b) study areas (gray circles), (c) geological map of Hawaria region, and (d) geological map of Zaghouan region: A-A—geologic sections.

Al_2O_3, their percentages were about 70 to 75%. The Al_2O_3 content was 19.01 and 18.25 wt % in the Ha_2 and Zg_3 samples, respectively, due to a relatively large amount of kaolinite. The amounts of alkaline-earth CaO and MgO ranged from 3 to 9%. These variations in the recorded quantities of the carbonates amounts for all crude clays are in agreement with the quantitative XRD analysis data. The amounts of alkaline oxides K_2O and Na_2O were high due to a relatively large amount of illite, especially, in the Ha_1 and Zg_2 samples. The low alkaline oxides rates for the Ha_2 and Zg_3 samples were an outcome of the kaolinite clays that have a low content of potassium and sodium. The high rates (5–7%) of Fe_2O_3 in the crude clays were associated with the Fe-rich illite and smectite under the Fe-oxide/hydroxide form. A high loss on ignition up to 10 wt % was due to a significant content of clay minerals and the amounts of carbonates in clays samples.

Fourier-Transform Infra-Red Spectroscopy

The FT-IR spectra of the crude samples revealed the presence of both clay and non-clay minerals,

Table 1. Mineralogical composition of raw materials (%)

Samples	Illite	Kaolinite	Smectite	Quartz	Feldesphar	Calcite	Dolomite
Ha_1	47	12	0	31	4	3	3
Ha_2	10	38	8	30	6	6	2
Ha_3	22	20	18	27	4	7	2
Zg_1	20	21	9	32	8	10	0
Zg_2	31	18	4	33	11	3	0
Zg_3	12	40	0	24	12	12	0

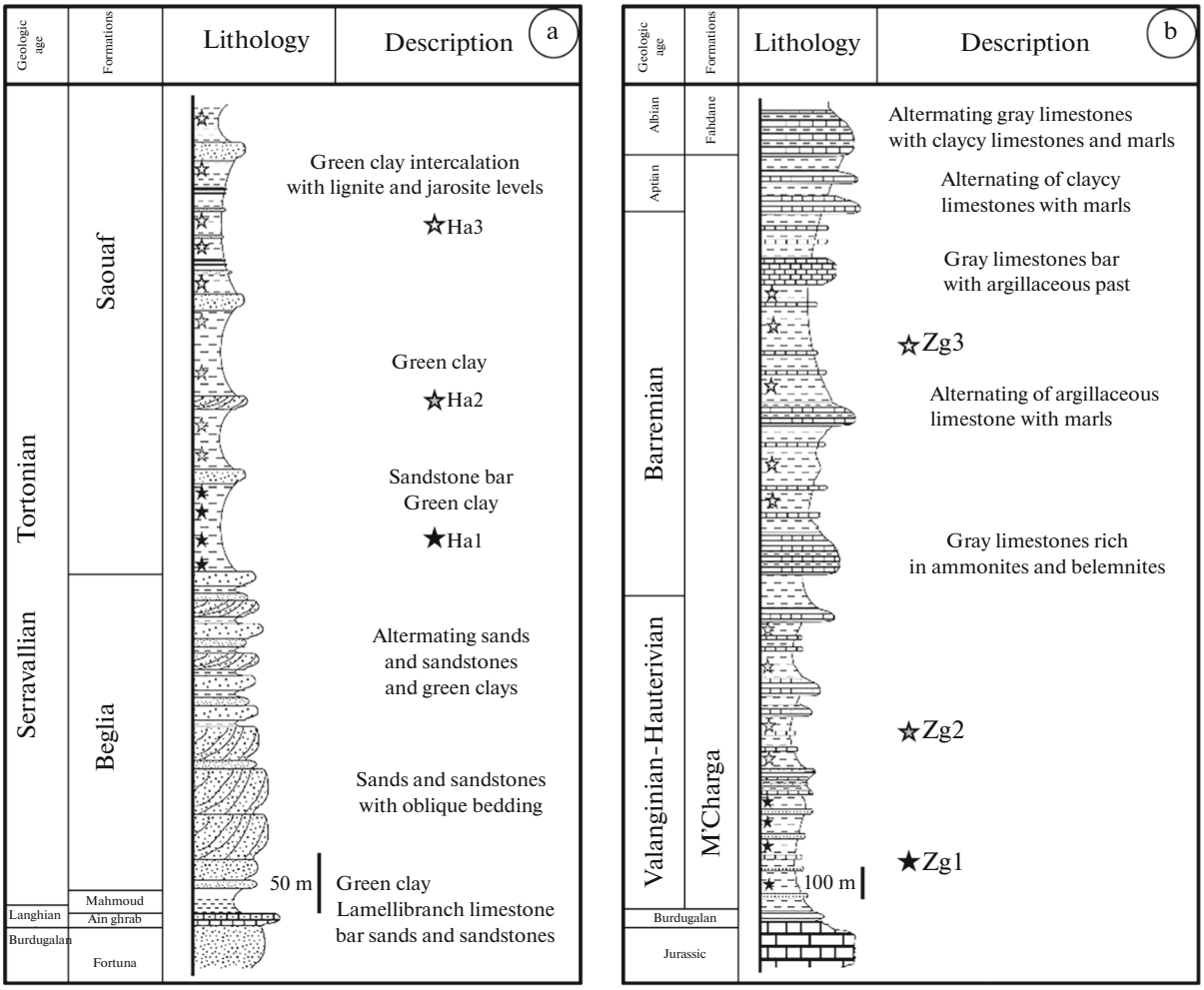

Fig. 2. Stratigraphic columns: (a) Hawaria region, and (b) Zaghouan region.

namely, illite, kaolinite, smectite, calcite, and quartz. The vibration bands corresponded to the illite structural OH stretching between 3618 and 3622 cm^{-1} (Fig. 4). The band of the kaolinite phase was observed at 3695 cm^{-1}. The bands at around 466 and 532 cm^{-1} were attributed to the Si–O–Si and Si–O–Al bending vibrations, respectively [22–24], whereas, the bands at around 694, 782, and 912 cm^{-1} originated from Mg, Fe–OH, Fe, Al–OH, Al, and Al–OH, respectively. The peaks ranging between 1420 and 1440 cm^{-1} were typical for the region characteristic for carbonate, which indicates the presence of carbonate anions. To be exact, the vibration bands at around 1010 and 1030 cm^{-1} arose from Si–O–Si [25, 26].

Table 2. Chemical composition (wt %) of raw clays

Samples	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO	CaO	LOI
Ha_1	55.37	17.54	5.51	0.2	2.99	1.96	1.54	13.56
Ha_2	52.48	19.01	6.95	0.35	2.29	2.25	3.78	11.41
Ha_3	53.64	17.57	5.09	0.57	2.45	2.08	5.08	12.16
Zg_1	58.24	16.45	4.81	0.34	2.36	1.84	4.76	10.15
Zg_2	56.34	15.94	5.67	0.53	3.46	2.45	1.02	13.34
Zg_3	53.34	18.25	5.54	0.67	1.34	2.45	7.16	10.08

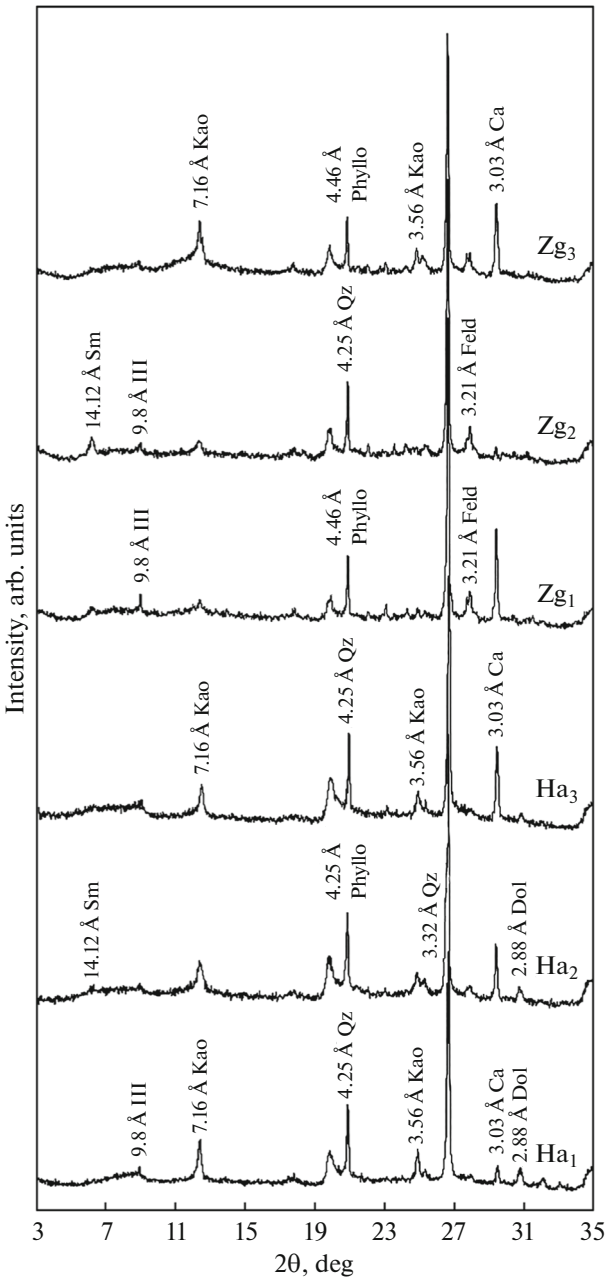

Fig. 3. XRD patterns of clay raw materials: Qz: quartz, Feld: feldspars, Ca: calcite, Dol: dolomite, Phyllo: phyllosilicate, Ill: illite, Kao: kaolinite, and Sm: smectite.

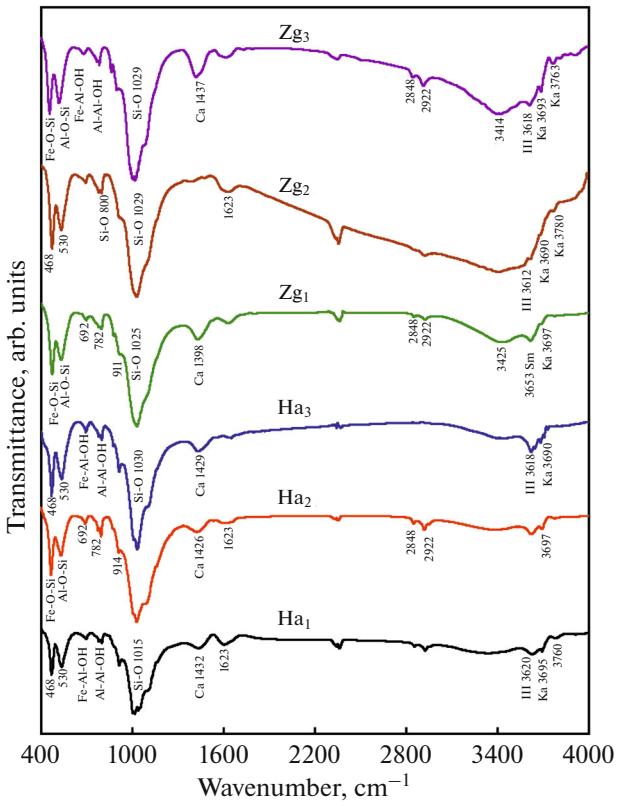

Fig. 4. FT-IR spectra of crude clays samples.

Particle Size Distribution

The grain size distribution of clay minerals is the main factor in determining the industrial applications orientation, which is especially important for finer particles. The particle size distribution of the studied raw materials indicates a silt dominated assemblage ranging from 66 to 72% (Table 3). Indeed, according to the smoothness of the grains, the ternary diagram (Fig. 5) demonstrates that the studied crude clays are classified as clayey silt. Clay minerals tend to have mostly particles of ∅ < 2 μm, but also they form agglomerations whose size is ∅ > 2 μm. The mineralogical parameter sand grain sizes classifications of the investigated raw clay suggest that a large amount of clay minerals is present in the silt fraction 2 < ∅ < 20 μm. The analyzed samples show a small variation in the grain sizes. The rates of the fractions that are less than 2 μm ranged from 25 to 31 wt %. The sand contents varied from 1 to 4 wt %.

Cation Exchange Capacity

The CEC values measured for the clay samples are in Table 4. The CEC values were approximately the same for the following samples: Ha_1, Ha_2, Zg_1, Zg_2, and Zg_3, varying from 19 to 23 meq/100 g), whereas the CEC value was higher for the Ha_3 sample (35 meq/100 g). These results revealed some differences mainly in the mineralogical composition of the crude samples. In some samples, smectite was either absent or present with very low rates.

Rheological Behavior

The clay suspensions viscosity is strongly affected by many factors: first, by the mineralogical composition and concentration of clay; second, by the size and shape of clay particles, and finally, by the exchange-

Table 3. Particle size distribution of raw materials

Samples	Clays	Silts			Sand
	∅ < 2	2 < ∅ < 20	20 < ∅ < 40	40 < ∅ < 63	63<
Ha_1	25	66	5	1	3
Ha_2	30	58	6	2	4
Ha_2	26	60	8	3	3
Zg_1	31	61	4	2	2
Zg_2	30	66	2	1	1
Zg_3	28	62	6	1	3

able ions [27, 28]. The measurements of the rheological parameter were carried out without any physical or chemical modification of the raw clays at room temperature. The flow behaviors were examined by the evaluation of shear rates. The used clay viscosity properties were correlated with the concentration of the solid rate in the suspension. All rheological tests were performed using different mass: 5 to 40 g of a clay mineral were added to 30 mL of distilled water. Before the rheological measurements, the clay suspension was agitated for 24 h. The viscosity curves of each clay sample indicated a non-Newtonian fluid with a dilatant behavior and a shear thickening model (Fig. 6). However, the behavior of the clay with distilled water was different for each sample. Certainly, the values of the viscosity increase with the solid mass/water ratio.

The rheological proprieties depend on the type of clay minerals that are present in the samples [29, 30]. The viscosity of the TOT structure clay minerals (T stands for the tetrahedral layer (mainly Si) and O stands for the octahedral layer (mainly Al)) increases significantly more than the TO structure minerals. For the clay suspensions containing smectite, especially for the Ha_3 sample, the hydration leads to the interlayer swelling and is associated with an increase in the volume suspension, which definitely results in a significant increase in viscosity. It almost reaches 8Pa at the clay mass of 40 g. For other samples, the rheological parameters were of the same order. However, the potential rheological parameter for the Ha_2 sample was low. This can be explained by a low illite rate that does not exceed 10%. Each illite particle with the TOT structure contains non-exchangeable K^+ interlayer cations and a permanent negative charge in the tetrahedral layers caused by the substitution of Si^{4+} ions with Al^{3+}. Weathering gradually transforms the illite mineral into an interstratified illite/smectite that can become a moderately swelling clay [31–33]. The calcium carbonate influence on the clay suspension rheological properties could be interpreted in different ways. For example, the sturdy aggregation prevents the clay dispersion, which was also demonstrated particu-

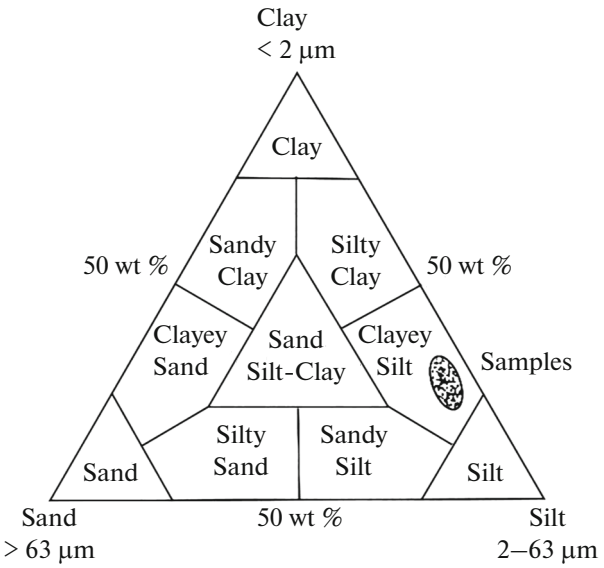

Fig. 5. Ternary diagram of clay/sand/silt proportions of clay samples.

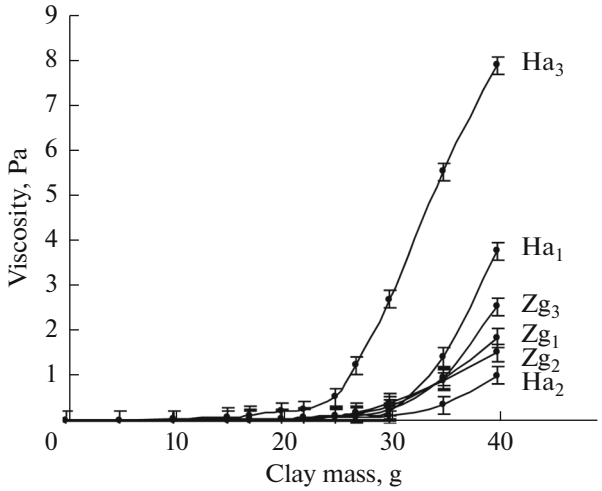

Fig. 6. Effects of clay composition on viscosity of suspension mixture in distilled water.

Table 4. CEC—meq/100 g of clay

Samples	Ha_1	Ha_2	Ha_3	Zg_1	Zg_2	Zg_3
CEC	22	23	35	20	23	19

larly by the Zg_1 and Zg_3 samples in Fig. 6. Therefore, the model dispersant as sodium carbonate is adsorbed strongly on the clay particles and allows the dispersion without affecting the clay particles properties. The clay suspensions with a higher solid content have the highest values of rheology due to a better orientation of clay particles and stronger repulsive force interactions [34–36].

Dispersion and the effect of the concentration of the dispersant Na_2CO_3 on the clay sedimentation, the effect of solid loading of the clay minerals powder and the rheological properties of the studies Tunisian clay were investigated and compared. The clay mass used for all rheological tests or the crucial mass was determined by extrapolating the linear part of the viscosity curve. The curial mass was used to evaluate the effect of the Na_2CO_3 addition on the rheological properties of each clay. All samples were agitated with distilled water to make a suspension of the desired density. The clay deflocculation by sodium carbonate was carried out by mixing clay suspension with an increasing amount of adjuvant. The suspensions were agitated during 48 hrs before the rheological measurements. The interactions between the clay minerals particles and Na_2CO_3, were investigated through viscosity using a rheometer. In fact, the amount of sodium carbonate was added to the clay mineral suspensions at different dosages of 0.05 to 1 vol % of the used clay mass. The rate of Na_2CO_3 added to the suspension was a function of the amount of clay with a mass ratio Na_2CO_3/clay. The insights that were derived from measuring the viscosity properties of the clay mineral suspensions containing a varying amount of Na_2CO_3 provide the foundation for many engineering applications and could optimize industrial processes. In fact, sodium carbonate, one of the most important dispersants used by addition to aqueous clay suspensions, plays a stabilizing role. One of the objectives of this work was to improve the rheological behavior of clay suspensions by introducing sodium carbonate as dispersant. The possible mechanisms of the interaction between the dispersant and the clay particles surfaces were investigated as well.

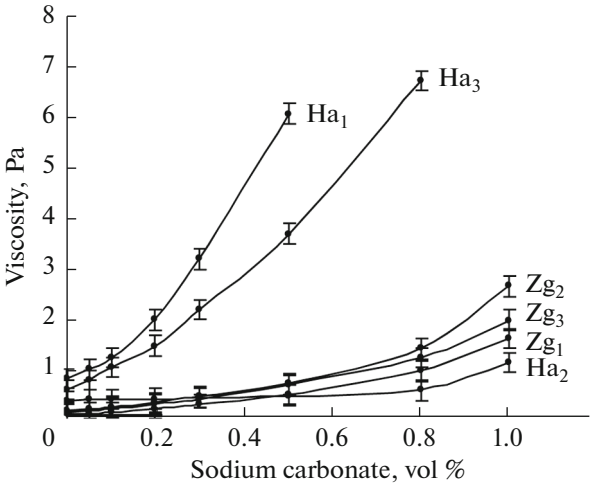

Fig. 7. Effect of Na_2CO_3 addition on viscosity of clay suspensions.

The addition of Na_2CO_3 shows a weak effect with a low concentration (0.05–0.3 vol %), but a strong impact with a high concentration (0.6–1 vol %). The rheological measurements showed viscosity increases at increasing the concentration of the added sodium carbonate (Fig. 7). This difference in rheological behavior of clays comes from the fact that sodium carbonate was added to the clay mineral suspensions in order to improve their rheological proprieties. However, this process causes a cation exchange between Na_2CO_3 and clay minerals [37]. Indeed, the Na^+ cation replaces Ca^{2+} in the interlayers, and the clay minerals become sodic. The presence of Na^+ in the interlayers space decreases the adhesive forces between the particles. Thus, the chemical bonds become low. Therefore, the dispersion and viscosity greatly increase. This process did not occur in the same way in all samples, as they differ in the rates of the dominant clay minerals, particularly those with the TOT structure. However, the Ha_1 and Ha_3 samples with high percentages of 47 and 40 wt %, respectively, present the best rheology values. For other samples, the dispersion was not adequate probably due to the presence of calcium carbonates. In fact, when calcium and magnesium were present in the suspensions at a high rate, they would participate in a reversible reaction by the substitution of Na^+ cation in the interlayer. The viscosity of the suspension would be greatly reduced. The rheological properties of the suspensions were improved by sodium carbonate addition: such as an increase in viscosity, a change in flow characteristics and suspensions flocculation. Those characteristics are of great significance in the manufacturing of many high performance ceramics by slip casting processing.

CONCLUSIONS

The purpose of this study was to determine the effect of the sodium carbonate on Tunisian clays and to use the mineralogical and geochemical characterization of clay minerals for a comprehensive understanding of the rheological behavior of clay minerals. The rheology tests were conducted on the raw clay suspensions and compared to the clay suspensions with added sodium carbonate. It provided a comparison of the rheological behavior of the clay structure

2 : 1 and the clay structure 1 : 1. The samples with a low rate of illite were at the lowest end of the rheograms, and they showed the lowest viscosities values. On the other hand, sample suspensions that contain smectite were found to have high viscosity values due to their hydration capacity as well as their easy dispersion. However, for the suspensions of the clay structure 1 : 1, the degrees of the layer links were so high that it was difficult to flocculate and stabilize the clay particles. On the other hand, the clay structure 2 : 1, especially smectite, with its hydration and surface charge properties, play a crucial role in the flocculating and stabilization of the clay suspensions. This proves that the extent of the difference is very evident in the rheological behavior of the clay minerals.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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